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Stimulated emission from vacuum-deposited thin films of a substituted oligo(*p*-phenylene vinylene)

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The influence of the morphology on the light emission properties of vacuum-deposited polycrystalline oligo(*p*-phenylene vinylene) thin films under intense laser excitation was studied. The morphology of the thin films was varied by annealing just below the first melting point (crystal-mesophase transition) and by crystallization from the isotropic melt. Amplified spontaneous emission occurred within the individual domains and was only observed when the domain size was increased by thermal treatment. The amplified spontaneous emission threshold for the melt-crystallized thin films was found to be comparable to that for conjugated polymer thin films. © *1998 American Institute of Physics.* [S0003-6951(98)01332-1]

Conjugated polymers like polythiophene (PT), poly[*p*-phenylene vinylene] (PPV) and derivatives, attract considerable attention nowadays for their potential use in thin-film microelectronics and optoelectronic devices. The latest challenge in this area of research is the possible development of an electrically pumped polymer laser. Lasing and amplified spontaneous emission (ASE) under pulsed optical excitation, using polymers as the active material, have already been demonstrated in solution,[1,2] and more recently, in neat thin films.[3–5] The most important question to be addressed is whether or not it is possible to obtain electrically induced stimulated emission and eventually net gain in conjugated polymers. Based on the lasing threshold under optical excitation, it is estimated[3] that current densities in excess of 10^6 A m^{-2} are needed to establish gain in such devices, which is much higher than currently attainable in polymer light-emitting diodes (LEDs). The low current densities in polymer LEDs, especially for electron transport, are the result of the low charge carrier mobilities, high trap densities, and poor charge injection in conjugated polymers. Oligomers could possibly provide the required properties for electrically pumped lasing. Conjugated oligomers, which can serve as model compounds[6–8] for their parent polymers, have a well-defined chemical structure and the potential ability to form well-ordered molecular assemblies. It is well known that ordered conjugated organic materials exhibit low trap densities and high charge carrier mobilities, for both electrons and holes. As an example, in single crystals of anthracene the hole and electron mobilities[9] are approximately 1 cm^2 V^{-1} s^{-1} and the crystal photoluminescence (PL) quantum yield at room temperature is almost unity. Both electroluminescence[9] and optically induced lasing[10] have been demonstrated in anthracene single crystals. The possibility to process oligomers into high-purity thin films by vacuum deposition allows the desired geometry for device application to be realized.

In this letter we report on stimulated emission (SE) from polycrystalline thin films of a 5-ring *n*-octyloxy-substituted oligo[*p*-phenylene vinylene] (Ooct-OPV5, Fig. 1) under intense laser excitation. The synthesis and characterization of Ooct-OPV5 have been described in a previous publication.[11] Thin films were prepared by slow evaporation on glass substrates just above the melting point (190 °C) and at a pressure of 10^{-6} mbar. Optical microscopy (Fig. 2) and atomic force microscopy showed that the as-deposited oligomer films were pinhole-free and exhibited a granular structure, indicating some extent of crystallinity. Annealing the film at a temperature of 120 °C resulted in a morphological change, which was irreversible. This morphological change manifested itself in an increase of the crystal domain size from approximately 4 to 20 μm. X-ray diffraction studies[11] on the as-deposited and annealed films confirmed the enhanced molecular order and the increase in crystal domain size upon

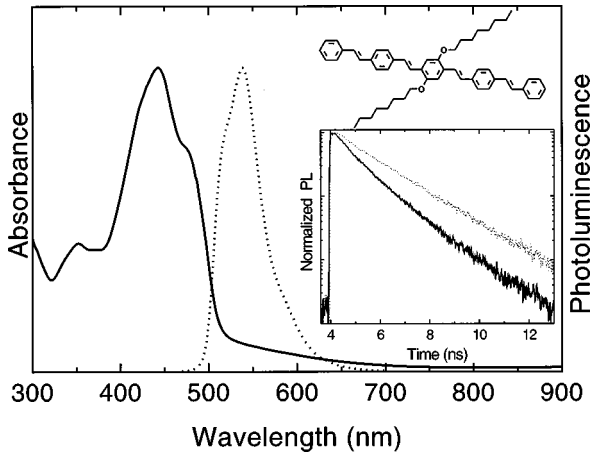

FIG. 1. Absorbance (solid line) and emission (dotted line) spectra of a vacuum-deposited Ooct-OPV5 film (thickness 300 nm) after annealing at 120 °C. Inset: the chemical structure of Ooct-OPV5 and PL-decay curves of a thin film, as deposited (solid line) and after annealing (dotted line).

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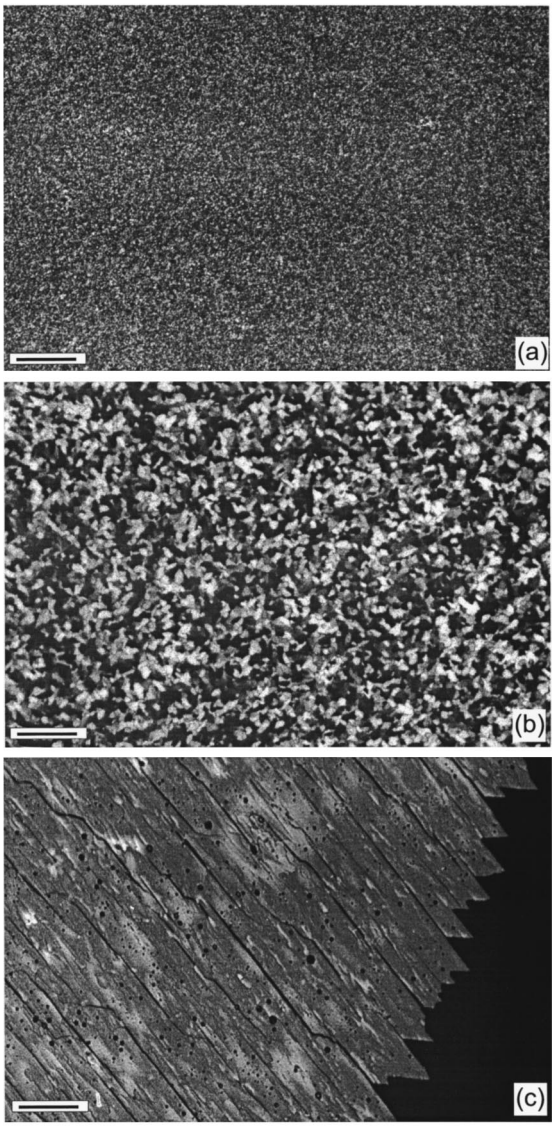

FIG. 2. Optical micrographs (crossed polarizers) of Ooct-OPV5 films. (a) as deposited, (b) after annealing at 120 °C, and (c) after crystallization from the isotropic melt at 210 °C. Scale bar is 100 μm.

annealing. Heating the film to the isotropic melt (210 °C) and subsequent slow cooling resulted in a different morphology (Fig. 2). Large domains were formed with dimensions up to several millimeters. The highly birefringent domains consisted of small bundles running parallel to the substrate. The exact microstructure of this morphology has not yet been revealed.

The absorbance (SLM Aminco 3000 Array spectrophotometer) and emission spectra (Perkin Elmer LS50-B spectrofluorometer) of an annealed Ooct-OPV5 film are shown in Fig. 1. Absolute photoluminescence quantum yields of approximately 0.5 were measured. The quantum yield increased from 0.5 to approximately 0.7 upon annealing and melt crystallization. PL decay curves of a vacuum-deposited film before and after annealing, obtained with the time-correlated single-photon counting technique, are depicted in Fig. 1 (inset). The increase in PL decay time after annealing and melt crystallization from $\tau = 1 \pm 0.2$ ns to 1.7 ± 0.2 ns agrees with the observed increase in quantum yield.

We have measured light emission spectra (Chromex 250 SI polychromator with Chromcam I CCD detector) from single crystals and thin films of Ooct-OPV5 under intense optical excitation with the third harmonic of a Nd:YAG laser (Quanta-Ray GRC 130-50, $\lambda = 355$ nm, pulse width 15 ns, repetition rate 1 Hz). For this study, thin films with a thickness of 300 nm were prepared by vacuum deposition onto glass substrates. The as-deposited films showed no spectral narrowing at any pump energy up to the damage threshold. Emission spectra at low and high excitation energies of an annealed Ooct-OPV5 film are shown in Fig. 3. At low excitation energy only the ordinary broad luminescence spectrum was observed, whereas above a well-defined excitation threshold a sharp emission peak (full width at half maximum ≈ 5 nm) appeared, centered around 550 nm and surrounded by a broad luminescence tail. The higher the excitation energy, the more dominant the spectrally narrowing emission became. The wavelength of the narrow peak at high pump energies coincides with the maximum of the luminescence emission spectrum.

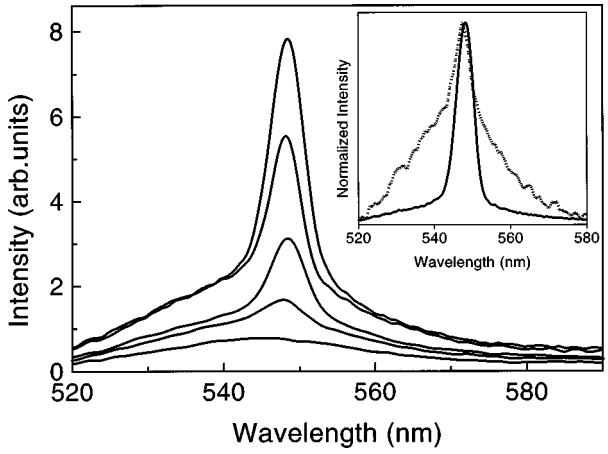

FIG. 3. Emission spectra of an annealed thin (300 nm) film of Ooct-OPV5. Excitation energy: 0.9, 1.6, 2.1, 3.1, and 3.9 mJ and excitation beam diameter ≈ 1.8 mm. Inset: emission spectra collected with a smaller spot size (diameter ≈ 30 μm) of the excitation beam. Excitation energy: 6 μJ (dotted line) and 180 μJ (solid line).

The integrated intensity and the linewidth of the total emission and of the narrow and broad emissions (deconvoluted from the total spectra) as a function of excitation energy are shown in Fig. 4. The observed appearance of a spectrally narrow peak above a well-defined energy threshold and the relative suppression (the sublinear growth) of the broad luminescence tails together with the linear dependence of the integrated total intensity, indicating the spectral energy redistribution within the emitted light, are a signature of light-induced net gain due to SE. The observed behavior can be explained in terms of ASE.

The energy threshold for linewidth collapse is approximately 1.6 mJ, which is three orders of magnitude higher than that of conjugated polymers.[3–5] This can be attributed to the polycrystalline structure of the thin films. We believe that ASE in the annealed films occurs only within the individual crystal domains, which on the average have dimensions of approximately 20 μm. Scattering at grain boundaries likely results in high optical losses, which prevents sufficient net gain to be realized over multiple domains. Hence, the amplification length is restricted by the size of the individual crys-

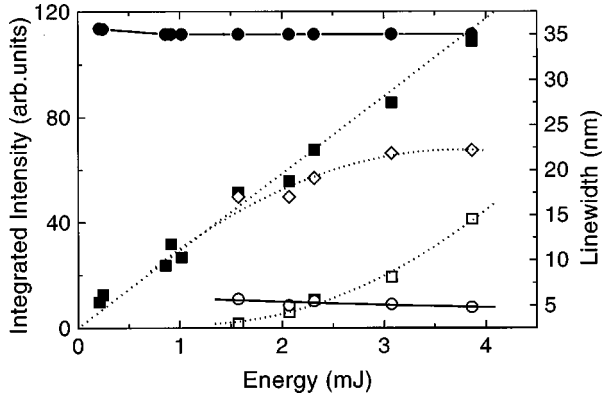

FIG. 4. Integrated intensity of total (filled squares), broad (open diamond), narrow (open squares), and linewidth of broad (filled circles) and narrow (open circles) emissions as a function of excitation energy for an annealed thin (300 nm) film of Ooct-OPV5.

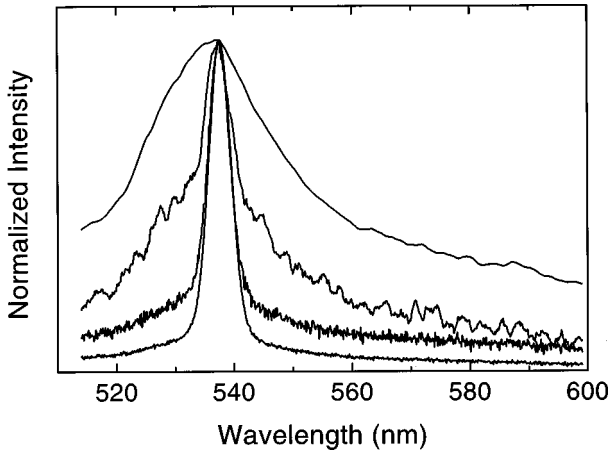

FIG. 5. Normalized emission spectra of a melt-crystallized thin (300 nm) film of Ooct-OPV5. Excitation energy: 1, 10, 50, and 70 μJ, excitation beam diameter ≈ 1 mm.

talline domains. Their size in as-deposited films, approximately 4 μm, is too small to achieve significant gain at all. Based on this argument one should expect that the threshold fluence for ASE in the case of the annealed Ooct-OPV5 films remains constant when the excitation spot size is decreased (down to a diameter comparable to the crystalline domain size ≈ 20 μm). This was checked by varying the excitation spot size, while maintaining approximately the same excitation fluence. A reduction of the excitation spot size from 1.8 to 1 mm did not alter the shape of the emission spectrum, which confirmed that the interaction length was significantly shorter than the diameter of the excited area. Additionally, a much smaller area of the films was excited by focusing the pump beam to a spot size with a diameter of approximately 30 μm. With such a beam size, at most, a few crystalline domains were excited and sample alignment was found to be crucial. ASE was not observed at each spot excited on the sample and the threshold of ASE varied highly from spot to spot, indicating that the excitation beam should be well aligned above a crystalline domain. The best results obtained from these experiments at low and high excitation energy (6 and 180 μJ, respectively) are shown in the inset of Fig. 3. Restricting the excitation area to only a few domains appears to result in a more pronounced relative suppression of the broad luminescence tail. The threshold fluence is roughly $100-200$ mJ cm^{-2}, which is a few times as high as that obtained with an excitation spot size of 1.8 mm. The excitation threshold observed with a spot diameter of 1.8 mm is mainly determined by the largest crystalline domains within roughly 10 000 illuminated by the beam. The probability of positioning the most favorable domain within an excitation spot having a diameter of roughly the size of a crystalline domain is extremely small, which explains the discrepancy between the threshold values.

Since the amplification length is restricted by the size of the crystalline domains, increasing the domain size will likely result in an ASE threshold comparable to that reported for conjugated polymer films, which are typically in the range of 10 μJ cm^{-2} to a few hundred μJ cm^{-2} using ns pulses. This was checked experimentally with Ooct-OPV5 films crystallized from the isotropic melt. The normalized emission spectra as a function of excitation energy for a melt-crystallized film are shown in Fig. 5. The lowest measured energy threshold for linewidth collapse was approximately 4 μJ, corresponding to a threshold fluence of ≈ 500 μJ cm^{-2}, which is substantially lower than that measured for the annealed films. Unlike in the annealed films, in the melt-crystallized ones the energy threshold was dependent on the excitation spot size at constant pump intensity, which indicated that amplification occurred over the whole illuminated area.

In conclusion, stimulated emission from vacuum-deposited polycrystalline thin films of a PPV oligomer has been demonstrated. In the case of the vacuum-deposited films, ASE occurs within the individual crystalline domains and was only observed after annealing or melt crystallization. The ASE threshold for an individual crystalline domain is comparable to that for conjugated polymer thin films.

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